

## Appendix A. Mass and Energy Balances

The basic mass- and energy balance equations solved by TOUGH2 can be written in the general form

$$\frac{d}{dt} \int_{V_n} M \, dV_n = \int_n \mathbf{F} \cdot \mathbf{n} \, d_n + \int_{V_n} q \, dV_n \quad (\text{A.1})$$

The integration is over an arbitrary subdomain  $V_n$  of the flow system under study, which is bounded by the closed surface  $n$ . The quantity  $M$  appearing in the accumulation term (left hand side) represents mass or energy per volume, with  $= 1, \dots, NK$  labeling the mass components (water, air,  $H_2$ , solutes, ...), and  $= NK + 1$  the heat “component.”  $\mathbf{F}$  denotes mass or heat flux (see below), and  $q$  denotes sinks and sources.  $\mathbf{n}$  is a normal vector on surface element  $d_n$ , pointing inward into  $V_n$ .

The general form of the mass accumulation term is

$$M = \sum S X \quad (\text{A.2})$$

The total mass of component is obtained by summing over the fluid phases ( $=$  liquid, gas, NAPL). is porosity,  $S$  is the saturation of phase (i.e., the fraction of pore volume occupied by phase ), is the density of phase , and  $X$  is the mass fraction of component present in phase . A more general form of the mass accumulation term that includes equilibrium sorption on the solid grains is given in Eq. (13). Similarly, the heat accumulation term in a multiphase system is

$$M^{NK+1} = (1 - )_R C_R T + \sum S u \quad (\text{A.3})$$

where  $_R$  and  $C_R$  are, respectively, grain density and specific heat of the rock,  $T$  is temperature, and  $u$  is specific internal energy in phase .

Advective mass flux is a sum over phases,

$$\mathbf{F} \big|_{\text{adv}} = \sum X \mathbf{F} \quad (\text{A.4})$$

and individual phase fluxes are given by a multiphase version of Darcy's law:

$$\mathbf{F} = \mathbf{u} = -k \frac{k_r}{\mu} (\nabla P - \mathbf{g}) \quad (\text{A.5})$$

Here  $\mathbf{u}$  is the Darcy velocity (volume flux) in phase ,  $k$  is absolute permeability,  $k_r$  is relative permeability to phase ,  $\mu$  is viscosity, and

$$P = P + P_c \quad (\text{A.6})$$

is the fluid pressure in phase , which is the sum of the pressure  $P$  of a reference phase (usually taken to be the gas phase), and the capillary pressure  $P_c$  ( $> 0$ ).  $\mathbf{g}$  is the vector of gravitational acceleration. Vapor pressure lowering due to capillary and phase adsorption effects is modeled by Kelvin's equation (Edlefsen and Anderson, 1943),

$$P_v(T, S_l) = f_{\text{VPL}}(T, S_l) \cdot P_{\text{sat}}(T) \quad (\text{A.7}),$$

where

$$f_{\text{VPL}} = \exp \left[ \frac{M_w P_{cl}(S_l)}{R(T + 273.15)} \right] \quad (\text{A.8})$$

is the vapor pressure lowering factor.  $P_{\text{sat}}$  is the saturated vapor pressure of bulk aqueous phase,  $P_{cl}$  is the difference between aqueous and gas phase pressures,  $M_w$  is the molecular weight of water, and  $R$  is the universal gas constant.

Heat flux includes conductive and convective components

$$\mathbf{F}^{\text{NK}+1} = - \nabla T + \sum h \mathbf{F} \quad (\text{A.9})$$

where is thermal conductivity, and  $h$  is specific enthalpy in phase . Radiative heat transfer according to the Stefan-Boltzmann law can also be modeled (see Eq. E.2).

Absolute permeability of the gas phase increases at low pressures according to the relation given by Klinkenberg (1941)

$$k = k_{\infty} \left( 1 + \frac{b}{p} \right) \quad (\text{A.10})$$

where  $k$  is the permeability at “infinite” pressure, and  $b$  is the Klinkenberg parameter. In addition to Darcy flow, mass transport can also occur by diffusion and hydrodynamic dispersion, as follows (de Marsily, 1986).

$$\mathbf{F} \big|_{\text{dis}} = - \sum \bar{\mathbf{D}} \nabla X \quad (\text{A.11})$$

The hydrodynamic dispersion tensor is given by

$$\bar{\mathbf{D}} = D_{,T} \bar{\mathbf{I}} + \frac{(D_{,L} - D_{,T})}{u^2} \mathbf{u} \mathbf{u} \quad (\text{A.12})$$

where

$$D_{,L} = \tau_0 d + \alpha_{,L} u \quad (\text{A.13a})$$

$$D_{,T} = \tau_0 d + \alpha_{,T} u \quad (\text{A.13b})$$

are longitudinal and transverse dispersion coefficients, respectively.  $d$  is the molecular diffusion coefficient for component in phase,  $\tau_0$  is the tortuosity which includes a porous medium dependent factor  $\tau_0$  and a coefficient that depends on phase saturation  $S$ ,  $\tau_0 = \tau_0(S)$ , and  $\alpha_{,L}$ ,  $\alpha_{,T}$  are the longitudinal and transverse dispersivities. Full hydrodynamic dispersion is included only in special versions of TOUGH2, while molecular diffusion in all phases is now part of the standard code. The mass flux from molecular diffusion alone is obtained by setting  $\alpha_{,L} = \alpha_{,T} = 0$  in Eq. (A.11 - A.13); diffusive flux of component in phase is given by (see Appendix D)

$$\mathbf{f} = - \tau_0 d \nabla X \quad (\text{A.14})$$

By applying Gauss’ divergence theorem, Eq. (A.1) can be converted into the following PDE

$$\frac{M}{t} = - \text{div } \mathbf{F} + q \quad (\text{A.15})$$

which is the form commonly used as the starting point for deriving finite difference or finite element discretization approaches. Of special interest is a simplified version of Eq. (A.15) for an approximate description of water seepage in the unsaturated zone. Neglecting phase change effects and assuming that the gas phase acts as a “passive bystander” with negligible gas pressure gradients, the following equation for liquid phase flow is obtained

$$\frac{\partial}{\partial t} S_l = \text{div} \left[ k \frac{k_{rl}}{\mu_l} \nabla (P_l + \rho_l g z) \right] \quad (\text{A.16})$$

Neglecting variations in liquid phase density and viscosity, as is appropriate for (nearly) isothermal conditions, Eq. (A.16) simplifies to Richards’ equation (1931)

$$\frac{\partial}{\partial t} S_l = \text{div} [K \nabla h] \quad (\text{A.17})$$

where  $S_l$  is specific volumetric moisture content,  $K = k k_{rl} \rho_l g / \mu_l$  is hydraulic conductivity, and  $h = z + P_l / \rho_l g$  is the hydraulic head.

## APPENDIX B. SPACE AND TIME DISCRETIZATION

The continuum equations (A.1) are discretized in space using the integral finite difference method (IFD; Edwards, 1972; Narasimhan and Witherspoon, 1976). Introducing appropriate volume averages, we have

$$\int_{V_n} M \, dV = V_n M_n \quad (\text{B.1})$$

where  $M$  is a volume-normalized extensive quantity, and  $M_n$  is the average value of  $M$  over  $V_n$ . Surface integrals are approximated as a discrete sum of averages over surface segments  $A_{nm}$ :

$$\int_n \mathbf{F} \cdot \mathbf{n} \, d = \sum_m A_{nm} F_{nm} \quad (\text{B.2})$$

Here  $F_{nm}$  is the average value of the (inward) normal component of  $\mathbf{F}$  over the surface segment  $A_{nm}$  between volume elements  $V_n$  and  $V_m$ . The discretization approach used in the integral finite difference method and the definition of the geometric parameters are illustrated in Fig. 60.

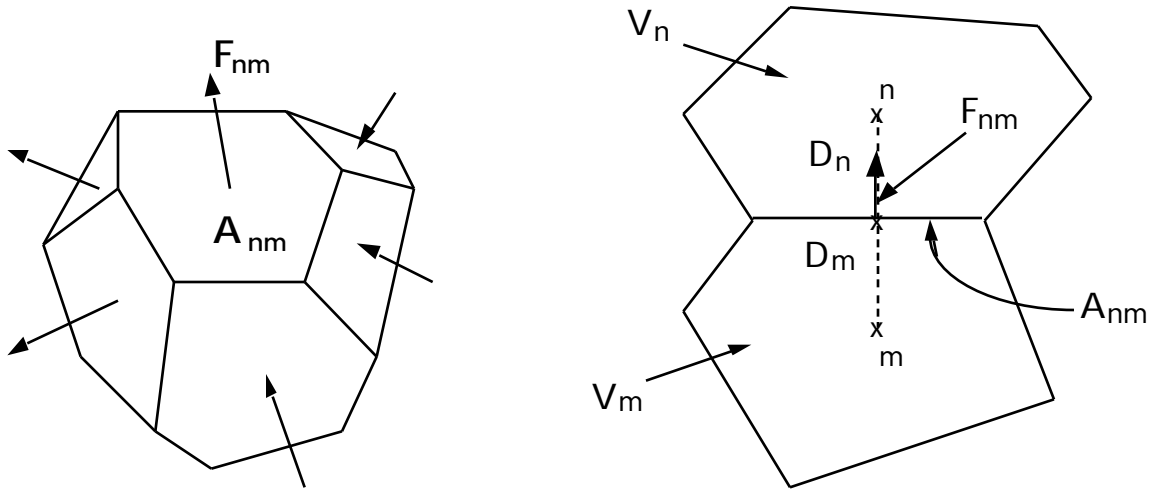


Figure 60. Space discretization and geometry data in the integral finite difference method.

The discretized flux is expressed in terms of averages over parameters for elements  $V_n$  and  $V_m$ . For the basic Darcy flux term, Eq. (A.5), we have

$$F_{,nm} = -k_{nm} \left[ \frac{k_r}{\mu} \right]_{nm} \left[ \frac{P_{,n} - P_{,m}}{D_{nm}} - g_{nm} \right] \quad (B.3)$$

where the subscripts (nm) denote a suitable averaging at the interface between grid blocks n and m (interpolation, harmonic weighting, upstream weighting).  $D_{nm} = D_n + D_m$  is the distance between the nodal points n and m, and  $g_{nm}$  is the component of gravitational acceleration in the direction from m to n. Discretization of diffusive fluxes raises some subtle issues and is discussed separately in Appendix D.

Substituting Eqs. (B.1) and (B.2) into the governing Eq. (A.1), a set of first-order ordinary differential equations in time is obtained.

$$\frac{dM_n}{dt} = \frac{1}{V_n} \sum_m A_{nm} F_{nm} + q_n \quad (B.4)$$

Time is discretized as a first-order finite difference, and the flux and sink and source terms on the right-hand side of Eq. (B.4) are evaluated at the new time level,  $t^{k+1} = t^k + \Delta t$ , to obtain the numerical stability needed for an efficient calculation of multiphase flow. This treatment of flux terms is known as “fully implicit,” because the fluxes are expressed in terms of the unknown thermodynamic parameters at time level  $t^{k+1}$ , so that these unknowns are only implicitly defined in the resulting equations (see, e.g., Peaceman, 1977). The time discretization results in the following set of coupled non-linear, algebraic equations

$$\begin{aligned} R_n^{,k+1} &= M_n^{,k+1} - M_n^{,k} - \frac{\Delta t}{V_n} \left\{ \sum_m A_{nm} F_{nm}^{,k+1} + V_n q_n^{,k+1} \right\} \\ &= 0 \end{aligned} \quad (B.5)$$

where we have introduced residuals  $R_n^{,k+1}$ . For each volume element (grid block)  $V_n$ , there are NEQ equations ( $n = 1, 2, \dots, \text{NEQ}$ ; usually,  $\text{NEQ} = \text{NK} + 1$ ), so that for a flow system with NEL grid blocks (B.5) represents a total of  $\text{NEL} \times \text{NEQ}$  coupled non-linear equations. The unknowns are the  $\text{NEL} \times \text{NEQ}$  independent primary variables  $\{x_i; i = 1, \dots, \text{NEL} \times \text{NEQ}\}$  which completely define the state of the flow system at time level  $t^{k+1}$ . These equations are solved by Newton/Raphson iteration, which is implemented as follows. We introduce an iteration index p and

expand the residuals  $R_n^{,k+1}$  in Eq. (B.5) at iteration step  $p + 1$  in a Taylor series in terms of those at index  $p$ .

$$R_n^{,k+1}(x_{i,p+1}) = R_n^{,k+1}(x_{i,p}) + \sum_i \frac{R_n^{,k+1}}{x_i} \bigg|_p (x_{i,p+1} - x_{i,p}) + \dots = 0 \quad (B.6)$$

Retaining only terms up to first order, we obtain a set of  $NEL \times NEQ$  linear equations for the increments  $(x_{i,p+1} - x_{i,p})$ :

$$- \sum_i \frac{R_n^{,k+1}}{x_i} \bigg|_p (x_{i,p+1} - x_{i,p}) = R_n^{,k+1}(x_{i,p}) \quad (B.7)$$

All terms  $R_n/x_i$  in the Jacobian matrix are evaluated by numerical differentiation. Eq. (B.7) is solved by sparse direct matrix methods (Duff, 1977) or iteratively by means of preconditioned conjugate gradients (Moridis and Pruess, 1995, 1998). Iteration is continued until the residuals  $R_n^{,k+1}$  are reduced below a preset convergence tolerance.

$$\left| \frac{R_{n,p+1}^{,k+1}}{M_{n,p+1}^{,k+1}} \right| \leq 1 \quad (B.8)$$

The default (relative) convergence criterion is  $\epsilon_1 = 10^{-5}$  (TOUGH2 input parameter RE1). When the accumulation terms are smaller than  $\epsilon_2$  (TOUGH2 input parameter RE2, default  $\epsilon_2 = 1$ ), an absolute convergence criterion is imposed,

$$|R_n^{,k+1}| \leq \epsilon_1 \cdot \epsilon_2 \quad (B.9).$$

Convergence is usually attained in 3 - 4 iterations. If convergence cannot be achieved within a certain number of iterations (default 8), the time step size  $\Delta t$  is reduced and a new iteration process is started.

It is appropriate to add some comments about our space discretization technique. The entire geometric information of the space discretization in Eq. (B.5) is provided in the form of a list of grid block volumes  $V_n$ , interface areas  $A_{nm}$ , nodal distances  $D_{nm}$  and components  $g_{nm}$  of gravitational acceleration along nodal lines. There is no reference whatsoever to a global system of

coordinates, or to the dimensionality of a particular flow problem. The discretized equations are in fact valid for arbitrary irregular discretizations in one, two or three dimensions, and for porous as well as for fractured media. This flexibility should be used with caution, however, because the accuracy of solutions depends upon the accuracy with which the various interface parameters in equations such as (B.3) can be expressed in terms of average conditions in grid blocks. A general requirement is that there exists approximate thermodynamic equilibrium in (almost) all grid blocks at (almost) all times (Pruess and Narasimhan, 1985). For systems of regular grid blocks referenced to global coordinates (such as  $r - z$ ,  $x - y - z$ ), Eq. (B.5) is identical to a conventional finite difference formulation (e.g., Peaceman, 1977; Moridis and Pruess, 1992).